Kinetics of Formation and Absorption Cross Sections of the ClO Dimer

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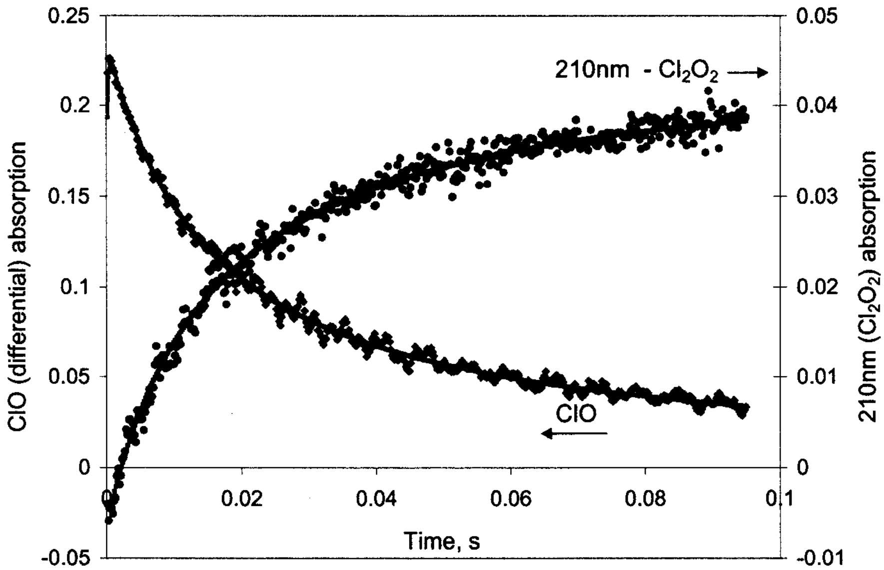
Chlorine oxide radicals are known to play a central role in the depletion of stratospheric ozone. The catalytic ozone destruction cycle involving the formation and photolysis of the ClO dimer has been calculated to account for the majority of the seasonal ozone depletion observed in the sunlit polar lower stratosphere. The efficiency of this catalytic cycle is limited by the self-reaction rate of ClO radicals, and the photolysis rate of the ClO dimer, Cl_2O_2:

	$ClO + ClO + M$	$\leftrightarrow$	$Cl_2O_2 + M$	(1)
	$ClOOCl + h\nu$	$\rightarrow$	$Cl + ClOO$	(2)
	$ClOO + M$	$\rightarrow$	$Cl + O_2 + M$	(3)
2×	$Cl + O_3$	$\rightarrow$	$ClO + O_2$	(4)

In this paper we report a kinetic study of the dimerisation of ClO radicals in which both ClO and Cl_2O_2 were monitored simultaneously *via* absorption spectroscopy. Such data determines both the ClO self-reaction rate coefficient, k_1, and in addition either the yield or the absorption cross section of Cl_2O_2.

The technique of flash photolysis with time-resolved UV absorption spectroscopy was employed, with a $Cl_2/Cl_2O/N_2$ precursor mixture. Three separate monochromator / PMT channels were used to follow the time-dependent evolution of ClO and Cl_2O_2. ClO radicals were quantified using the differential spectroscopy technique, *via* simultaneous measurements of the ClO absorption at the (12,0) band peak and the adjacent valley of the ($A \leftarrow X$) transition at approximately 275nm. The third detection channel was used to monitor the formation of Cl_2O_2 at 210nm. The apparatus has been described in detail elsewhere.[1] Supporting experiments which determined the temperature-dependent ClO differential cross section and investigated the possible formation of the asymmetric ClO dimer, ClOClO, were also performed using an OMA detection system. Experiments were conducted between 183 and 250K, at 15-700 Torr total pressure. Typical ClO and Cl_2O_2 kinetic traces and optimised fits are shown in the figure below:



The negative temperature-dependence of the differential ClO cross-section was found to be more pronounced at very low temperatures (<200K) than extrapolation of previous results[2] suggests. Consequently, the dimerisation of ClO radicals was found to proceed with a rate coefficient (k_1) some 25% higher than the current evaluation[3] at very low temperatures. The value obtained for $\sigma(Cl_2O_2)$ was consistent with the current evaluation. No evidence for formation of ClOClO was observed.

1. Nickolaisen, S.L. *et al.*, *J. Phys. Chem.* **104**, 308-319, 2000.
2. Sander, S.P. & R.R. Friedl, *J. Phys. Chem.* **93**, 4764-4771, 1989.
3. NASA - JPL Evaluation #13: *JPL Publication 00-3*, 2000.

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